



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08K 5/098, C08L 45/00, B32B 27/08,</b> <b>A23L 3/3436</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/06779</b> <b>(43) International Publication Date:</b> 19 February 1998 (19.02.98)
<b>(21) International Application Number:</b> PCT/US97/13015 <b>(22) International Filing Date:</b> 24 July 1997 (24.07.97)  <b>(30) Priority Data:</b> 08/698,011                      13 August 1996 (13.08.96)                      US  <b>(71) Applicant:</b> CHEVRON CHEMICAL COMPANY [US/US]; 555 Market Street, San Francisco, CA 94105 (US).  <b>(72) Inventors:</b> KATSUMOTO, Kiyoshi; 2615 Brooks Avenue, El Cerrito, CA 94530 (US). CHING, Ta, Yen; 10 Santa Yorma Court, Novato, CA 94945 (US).  <b>(74) Agents:</b> MICHEL, Marianne, H. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> MULTI-COMPONENT OXYGEN SCAVENGING COMPOSITION		
<b>(57) Abstract</b>  An oxygen scavenging composition or system is provided comprising at least one polyterpene and at least one catalyst effective in catalyzing an oxygen scavenging reaction. A film, a multi-phase composition, a multi-layer composition, an article comprising the oxygen scavenging composition, a method for preparing the oxygen scavenging composition, and a method for scavenging oxygen are also provided.		

1           **MULTI-COMPONENT OXYGEN SCAVENGING COMPOSITION**

2    This application is a continuation-in-part of co-pending application Serial  
3    No. 08/388,815 filed February 15, 1995.

4                           Background of the Invention

5    The present invention relates to an oxygen scavenging composition or system  
6    which can be employed in films, multi-layer films, sheets and molded or  
7    thermoformed shapes that find utility in low oxygen packaging for  
8    pharmaceuticals, cosmetics, oxygen sensitive chemicals, electronic devices, and  
9    food.

10   Organic oxygen scavenging materials have been developed partly in response to  
11   the food industry's goal of having longer shelf-life for packaged food.

12   One method which is currently being employed involves the use of "active  
13   packaging" where the package is modified in some way so as to control the  
14   exposure of the product to oxygen. Such "active packaging" can include sachets  
15   containing iron based compositions such as AGELESS<sup>TM</sup> which scavenges  
16   oxygen within the package through an oxidation reaction. However, such an  
17   arrangement is not advantageous for a variety of reasons including the  
18   accidental ingestion of the sachets or the oxygen-scavenging material present  
19   therein.

20   Other techniques involve incorporating an oxygen scavenger into the package  
21   structure itself. In such an arrangement, oxygen scavenging materials constitute  
22   at least a portion of the package, and these materials remove oxygen from the  
23   enclosed package volume which surrounds the product or which may leak into

1 It is another object of the present invention to provide a composition which  
2 produces reduced levels of oxidation by-products.

3 It is another object of the present invention to provide an article, package or  
4 container suitable for oxygen scavenging.

5 It is another object of the present invention to provide a method for preparing an  
6 oxygen scavenging composition.

7 It is another object of the present invention to provide a method for scavenging  
8 oxygen.

9 According to the present invention, an oxygen scavenging composition or system  
10 is provided comprising at least one polyterpene and at least one catalyst  
11 effective in catalyzing the oxygen scavenging reaction. A film, a multi-phase  
12 composition, a multi-layer composition, an article comprising the oxygen  
13 scavenging composition, a method for preparing the oxygen scavenging  
14 composition, and a method for scavenging oxygen are also provided.

15 Brief Description of the Drawings

16 Figure 1 graphically shows the oxygen scavenging performance of an oxygen  
17 scavenging composition comprising 30% polyterpene and 70% polyethylene.

18 Figures 2-4 show by bar graphs the relative amounts of specific aldehydes  
19 produced from examples containing blends of polyethylene with polyterpene,  
20 styrene/butadiene block copolymer, polybutadiene, or polyoctenamer.

21 Figure 5 shows the relative amounts of specific acids produced from examples  
22 containing blends of polyethylene with polyterpene, styrene/butadiene block  
23 copolymer, polybutadiene, or polyoctenamer.

1 The polyterpene can be blended with a carrier resin comprising other oxidizable  
2 polymers or polymers having a slower oxidation rate than the polyterpene.

3 Examples of other oxidizable polymers include substituted or unsubstituted  
4 ethylenically unsaturated hydrocarbons such as polybutadiene, polyisoprene,  
5 and styrene-butadiene block copolymers. Other examples include those  
6 described in U.S. Pat. Nos. 5,211,875 and 5,346,644 to Speer et al., which are  
7 hereby incorporated by reference in their entirety. Other examples include  
8 poly(meta-xylenediamine-adipic acid) (also known as MXD6), acrylates which  
9 can be prepared by transesterification of poly(ethylene-methyl acrylate) such as  
10 poly(ethylene-methyl acrylate-benzyl acrylate), poly(ethylene-methyl acrylate-  
11 tetrahydrofurfuryl acrylate), poly(ethylene-methyl acrylate-nopol acrylate) and  
12 mixtures thereof. Such transesterification processes are disclosed in 08/475,918  
13 filed June 7, 1995, the disclosure of which is hereby incorporated by reference.

14 In a preferred embodiment, the carrier resin oxidizes at a slower rate than the  
15 polyterpene. Oxygen scavenging compositions prepared from such carrier  
16 resins produce reduced amounts of migratory oxidation by-products such as low  
17 molecular weight aldehydes, alkenes and carboxylic acids.

18 Typical examples of carrier resins exhibiting a slower oxidation rate include  
19 polyesters, polyaromatics, or polyolefin homopolymers, copolymers, or  
20 terpolymers. Specific examples of polymers exhibiting a slower oxidation rate  
21 include polyethylene, low density polyethylene, high density polyethylene, linear  
22 low density polyethylene, polystyrene, as well as copolymers such as  
23 poly(ethylene-vinyl acetate), poly(ethylene-methyl acrylate), poly(ethylene-ethyl  
24 acrylate), poly(ethylene-butyl acrylate), and ionomers of poly(ethylene-methyl  
25 acrylate), poly(ethylene-ethyl acrylate), or poly(ethylene-acrylic acid).

1 The oxygen scavenging composition can be activated by methods known in the  
2 art such as ultraviolet, e-beam, or thermal triggering. Preferably, the composition  
3 is activated with 0.2-5 J/cm<sup>2</sup> of UV radiation in the range of from 250-400 nm. A  
4 photoinitiator is useful for decreasing the catalyst activation time. Effective  
5 photoinitiators include those known in the art.

6 In another aspect of the invention, the oxygen scavenging composition  
7 comprises a first phase comprising the polyterpene and a second phase  
8 comprising the catalyst. The first phase is essentially devoid of catalyst. The  
9 second phase is in sufficiently close proximity to the first phase to catalyze the  
10 oxygen scavenging reaction. When the polyterpene and the catalyst are in  
11 separate phases, processing difficulties, such as deactivation of the catalyst, are  
12 avoided.

13 In another aspect of the invention, the catalyst is incorporated into a polymeric  
14 material to form at least one catalyst-containing layer. In such a case, the  
15 catalyst-containing layer can be situated between the package contents and an  
16 oxygen scavenging layer or between the outside of the package and the oxygen  
17 scavenging layer. Also, the catalyst layer can be located between two oxygen  
18 scavenging layers or the oxygen scavenging layer can be located between two  
19 catalyst layers.

20 In another aspect of the invention, the oxygen scavenging composition or system  
21 can include a polymeric selective barrier layer. The selective barrier layer  
22 functions as a selective barrier to certain oxidation by-products, but not to  
23 oxygen itself. Preferably, the layer prevents at least half of the number and/or  
24 amount of oxidation by-products having a boiling point of at least 40°C from  
25 passing through the polymeric selective barrier layer.

## Examples

Blends of various resins were prepared as follows.

In Run 101, 350 g PE 1017 resin from Chevron (low density polyethylene) and 150 g Piccolyte C115 resin from Hercules (polylimonene) were melt blended at 170°C to give a blend of 70 weight percent polyethylene and 30 weight percent Piccolyte. Figure 1 demonstrates the oxygen scavenging properties at 4°C of the thus produced blend of Run 101. The percent oxygen in a closed 300 cc headspace was measured on various days. The sample size was 0.25 g.

In Run 102, a blend of 90 weight percent Vector 8508D resin from Dexco(styrene/butadiene block copolymer) and 10 weight percent PE 1017 was prepared.

In Run 103, a blend of 54 weight percent Taktene 1202 rubber from Bayer (polybutadiene) and 36 weight percent PE 1017 was prepared.

In Run 104, a blend of 30 weight percent Vestenamer resin from Huls (polyoctenamer) and 70 weight percent PE 1017 was prepared.

The blends also contained 1000 ppm by weight Irganox 1076, and 1000 ppm by weight cobalt oleate. The blends were extruded into 1-1.5 mil thick films. The film samples were irradiated with a Blak-Ray UV lamp (254 nm, 5 mW/cm<sup>2</sup>) for 1 minute. Film samples were 1 inch away from the UV lamps. A predetermined amount of samples of the thus prepared films was individually placed in 2" x 30" glass tubes and purged at 20-25°C with 10-15 mL/min. one percent oxygen. The gas was trapped in 3 stages, trap 1 — ice bath, trap 2 — dry ice and acetone, and trap 3 — bubbled gas through water. The trapped gases from the samples were analyzed using gas chromatography and mass spectrometry.

1 WHAT IS CLAIMED IS:

- 2 1. An oxygen scavenging composition comprising at least one polyterpene  
3 and at least one catalyst effective in catalyzing oxygen scavenging.
- 4 2. The oxygen scavenging composition according to claim 1, wherein the  
5 polyterpene comprises poly(alpha-pinene), poly(beta-pinene),  
6 poly(dipentene), poly(d-limonene), or poly(d,l-limonene).
- 7 3. The oxygen scavenging composition according to claim 1 which exhibits  
8 reduced amounts of oxidation by-products compared to substituted or  
9 unsubstituted ethylenically unsaturated hydrocarbon polymers.
- 10 4. The oxygen scavenging composition according to claim 1 wherein the  
11 polyterpene is present in an amount in the range of from about 5 weight  
12 percent to about 95 weight percent based on the total oxygen scavenging  
13 composition.
- 14 5. The oxygen scavenging composition according to claim 4 wherein the  
15 polyterpene is present in an amount in the range of from about 10 weight  
16 percent to about 75 weight percent based on the total oxygen scavenging  
17 composition.
- 18 6. The oxygen scavenging composition according to claim 5 wherein the  
19 polyterpene is present in an amount in the range of from 15 weight percent  
20 to 50 weight percent based on the total oxygen scavenging composition.
- 21 7. The oxygen scavenging composition according to claim 1 further  
22 comprising at least one carrier resin.

- 1    15. The oxygen scavenging composition according to claim 11 wherein the  
2        carrier resin is present in an amount in the range of from 50 weight percent  
3        to 85 weight percent based on the total oxygen scavenging composition.
- 4    16. The oxygen scavenging composition according to claim 1, wherein the  
5        catalyst is a transition metal salt.
- 6    17. The oxygen scavenging composition according to claim 16, wherein the  
7        catalyst is a cobalt salt.
- 8    18. The oxygen scavenging composition according to claim 17, wherein the  
9        catalyst is cobalt oleate, cobalt linoleate, cobalt neodecanoate, cobalt  
10       stearate, or cobalt caprylate.
- 11   19. The oxygen scavenging composition according to claim 1 further  
12       comprising a photoinitiator.
- 13   20. The oxygen scavenging composition according to claim 1 wherein the  
14       carrier resin comprises an oxidizable polymer.
- 15   21. The oxygen scavenging composition according to claim 20 wherein the  
16       oxidizable polymer is a substituted or unsubstituted ethylenically  
17       unsaturated hydrocarbon polymer.
- 18   22. The oxygen scavenging composition according to claim 21 wherein the  
19       oxidizable polymer is polybutadiene, polyisoprene, poly(styrene-butadiene),  
20       poly(meta-xylenediamine-adipic acid), or polyacrylates which can be  
21       prepared by transesterification of poly(ethylene-methyl acrylate) including  
22       poly(ethylene-methyl acrylate-benzyl acrylate), poly(ethylene-methyl  
23       acrylate-tetrahydrofurfuryl acrylate), poly(ethylene-methyl acrylate-nopol  
24       acrylate), or mixtures thereof.



- 1    33.    The article of claim 29 wherein the article is a patch, bottle cap insert or  
2           molded or thermoformed shape.
- 3    34.    The article of claim 33 wherein the molded or thermoformed shape is a  
4           bottle or tray.
- 5    35.    A method for scavenging oxygen comprising placing an oxygen-sensitive  
6           product in the package of claim 27.
- 7    36.    A method for preparing an oxygen scavenging composition comprising melt  
8           blending at least one polyterpene and at least one catalyst effective in  
9           catalyzing oxygen scavenging.
- 10   37.    The method of claim 36 further comprising melt blending at least one  
11           carrier resin in the oxygen scavenging composition, wherein the carrier  
12           resin exhibits a slower oxidation rate than the polyterpene.
- 13   38.    The method of claim 37 further comprising at least one photoinitiator.

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ALDEHYDES vs. Primary Oxidizable Component  
Relative Concentration of Compound by GC-MS

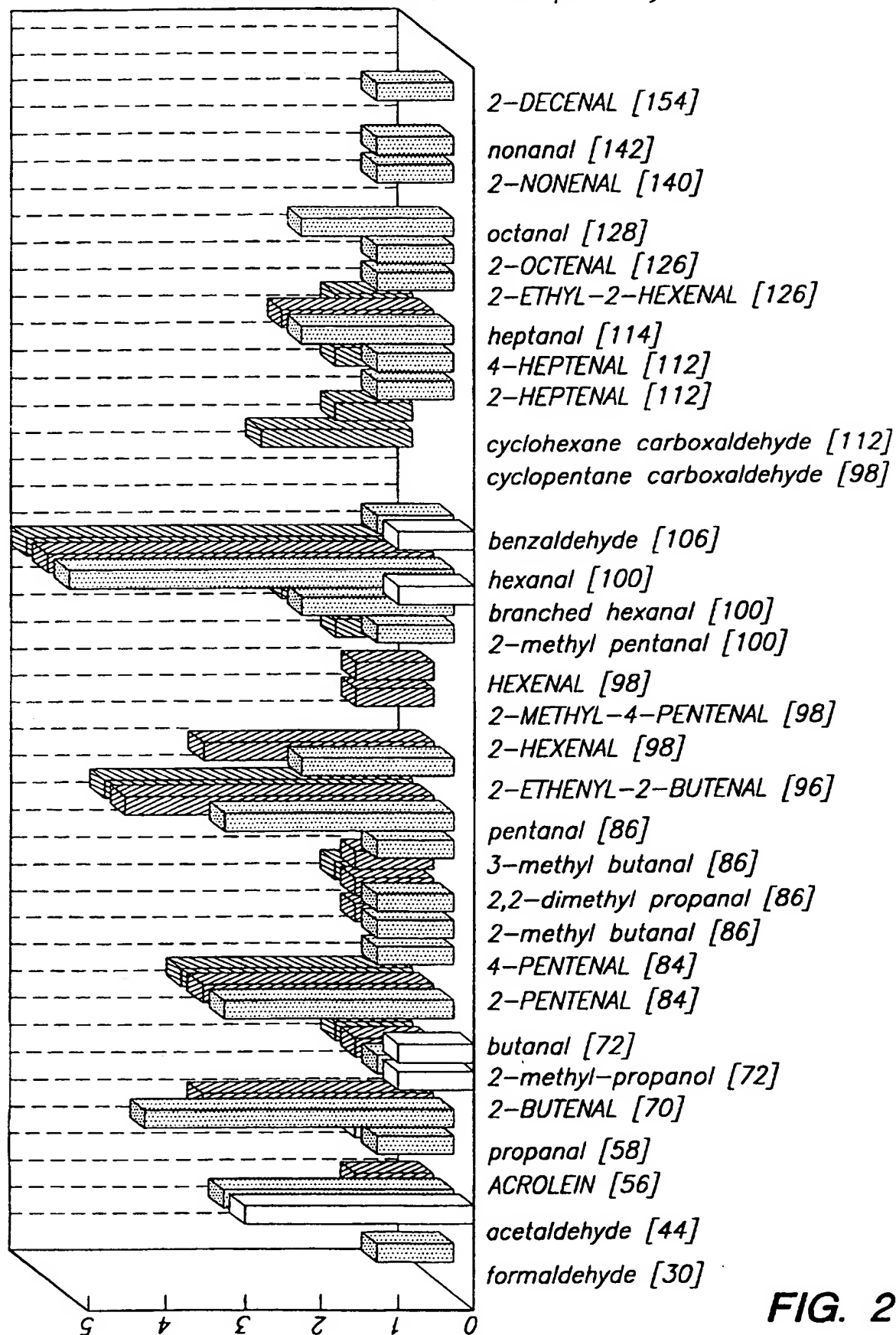


FIG. 2

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## ALDEHYDES vs. Primary Oxidizable Component

Relative Concentration of Compound by GC-MS

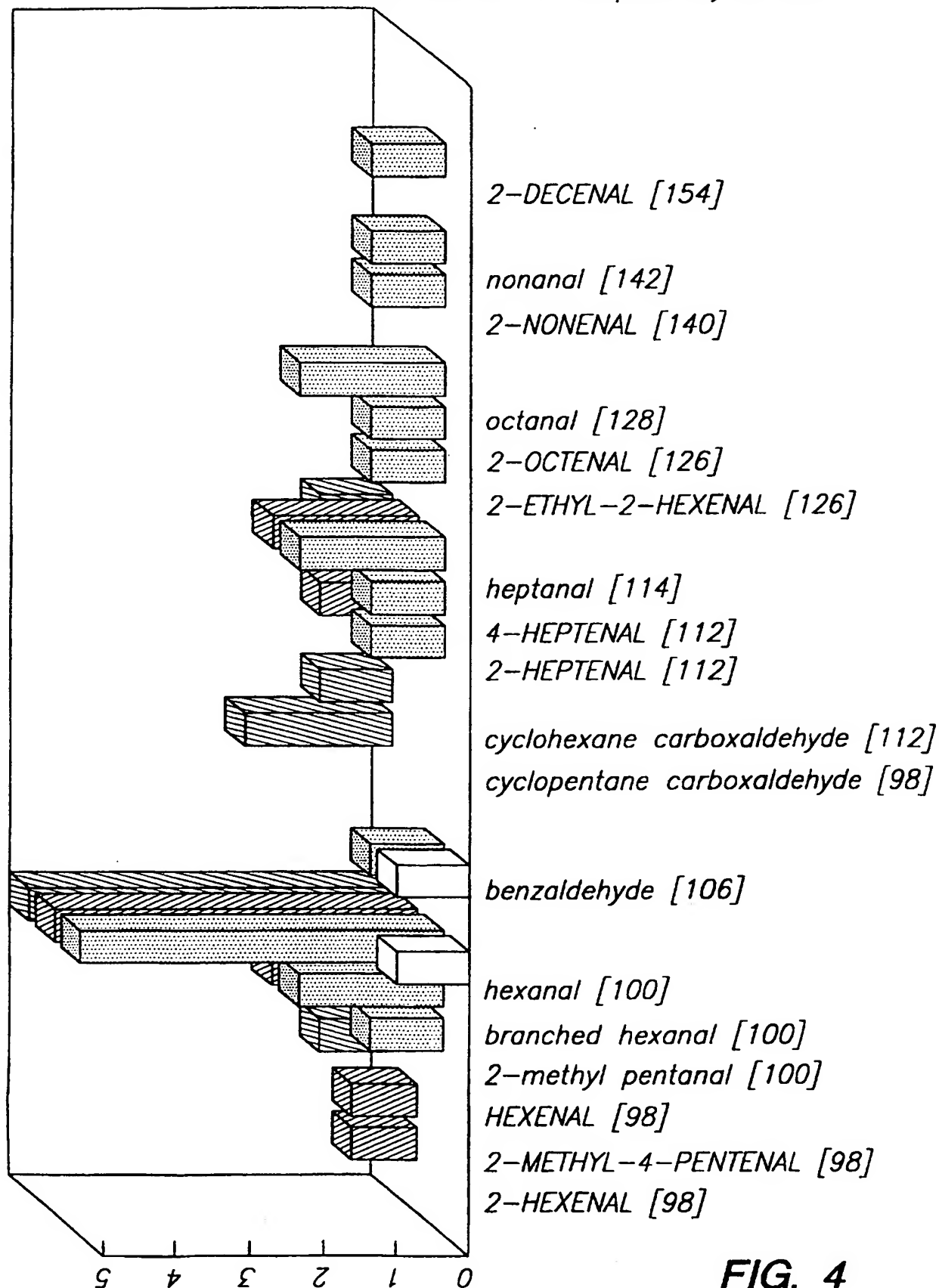
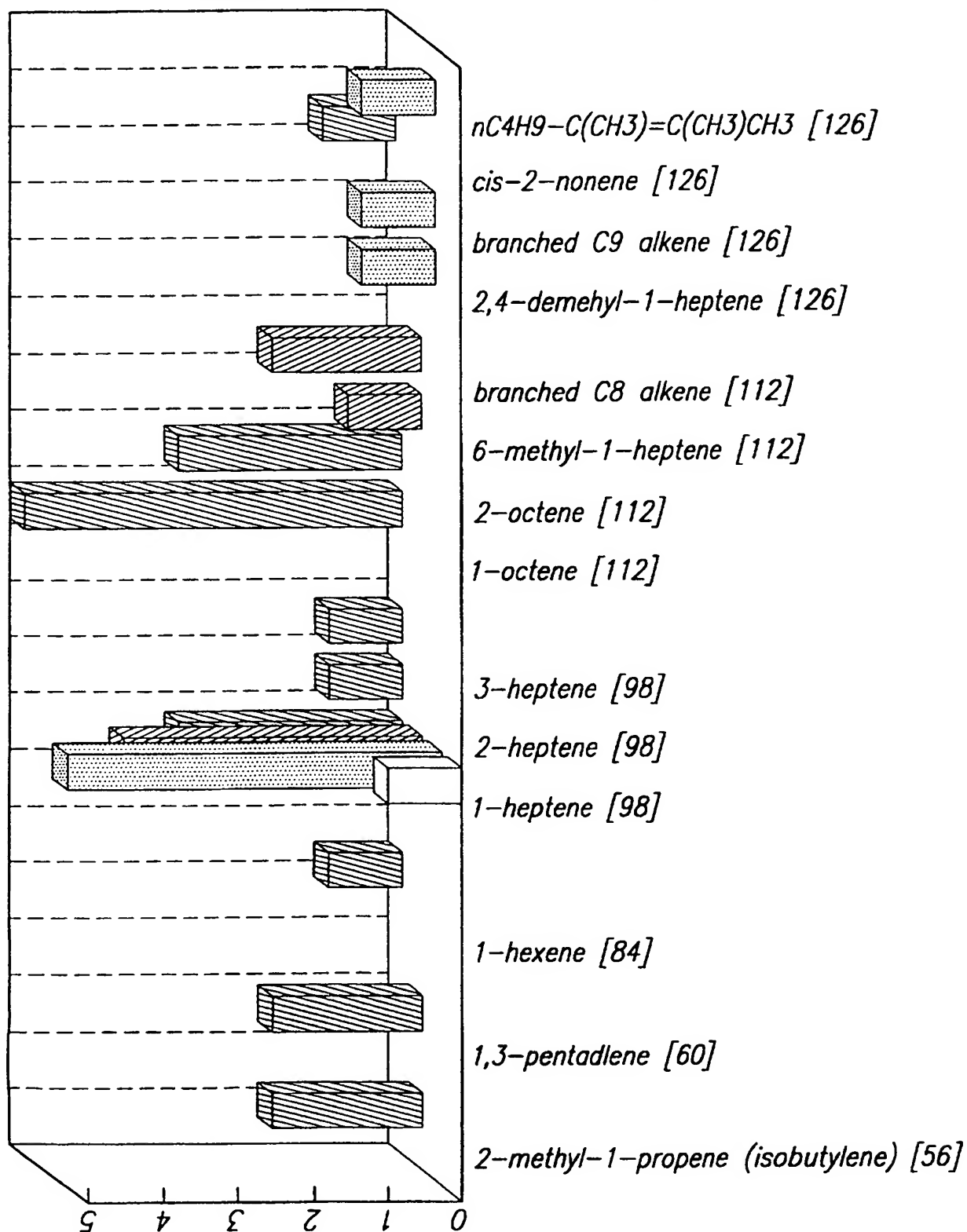


FIG. 4

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**FIG. 6***ALKENES vs. Primary Oxidizable Component**Relative Concentration of Compound by GC-MS*

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/13015

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